

Material Behaviour

The effect of Pb and other elements found in recycled polypropylene on the manufacturing of lead-acid battery cases

E.E. Ferg*, N. Rust

Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth 6031, South Africa

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Abstract

Polypropylene (PP) is one of the most common plastics used in the manufacturing of lead-acid battery cases, where the recycling of the material has become common practice, being both economically viable and environmentally friendly. During the recycling process, the various components of the spent battery are separated, where the crushed battery case is washed in order to remove any excess acid and lead-containing particles. The plastic components are subsequently melted and extruded into pellets that are then blended with virgin material to injection mold new battery cases and lids. This study showed that a significant amount of lead-containing particles in the form of lead dioxide and lead sulfate remain in the recycled plastic, and are evenly distributed throughout the polymer matrix. TEM studies showed that the particles are less than 1 μm in size and X-ray diffraction analysis of ashed recycled PP samples showed the presence, amongst others, of talc, calcium carbonate, rutile and iron oxide. These compounds come from a range of fillers, flame-retardants, colorants and impurities that originated from the various original battery cases that were recycled. The study showed that modern X-ray fluorescence (XRF) analysis is a quick and reliable method to quantify the amount of the elements found in the plastic and that the concentration of Pb in the plastic can be used as a type of “tracer” to determine the amount of recycled PP used in the manufacturing of a particular battery case. The study also showed that there is possible environmental contamination, in particular with Pb and Br contained in recycled PP during the injection molding process and the burning of the plastic. The Pb- and Br-containing particles are small enough to become air-borne during the burning process of the plastic, resulting in them being part of the soot and other hydrocarbon oils that are emitted. No Pb was observed in the gases emitted during simulated low-temperature injection molding conditions; however, a significant amount of Br was detected in the gases at the lower temperatures. Clear environmental waste classification of the battery case plastic should be done before its final incineration where the amount of trace metals present and its possible contamination to the environment should be considered. Care should also be taken for machine operators who work with the recycled plastic, that no excessive exposure to the halogenated compounds is experienced.

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1. Introduction

Polypropylene (PP) has become one of the most common plastics used in the manufacturing of automotive and some industrial lead-acid battery

*Corresponding author. Tel.: +27 41 504 3160;
fax: +27 86 519 3597.

E-mail address: ernst.ferg@nmmu.ac.za (E.E. Ferg).

casings. Before the commercialization of PP as battery case material, the outer casings of lead-acid batteries were made from synthetic rubber, while some of the casings of large industrial batteries were even made from silica glass. Since the early 1970s, PP has been used for almost all shapes and sizes of lead-acid battery casings and lids, especially for the automotive portable batteries [1]. In general, the properties of PP are well suited for their use as battery case material, where it can withstand the harsh environmental conditions under particular applications. These include a wide temperature range (-32 to 80°C); chemical resistance to acid, fuel, oils and antifreeze; physical shock; good elasticity and low mold shrinkage to accommodate other material components such as lead post terminals.

Due to the short life-span of a typical automotive battery (2–4 years) and with the increase of its end-user consumption, stricter environmental legislation was introduced concerning its use, disposal and the recycling of heavy metals such as lead (Pb). This has resulted in the complete recycling of the battery in terms of its content where the Pb alloy, oxide and sulfate materials are regenerated for their reuse in electrode manufacturing. The electrolyte or acid is neutralized and the battery case housing is recycled and reused for the manufacturing of battery cases. The recycling of the complete battery has become very efficient where up to 90% of the batteries manufactured are returned and the recycling loop is well managed in most countries that have lead-acid battery manufacturers [2,3].

The recycling process of the lead-acid battery starts at the point where the old battery is returned to the distributor. The batteries are crushed using toothed stainless-steel rollers where the Pb, PP casings and polyethylene separators are separated by floatation due to their respective differences in densities. The heavier lead fraction is removed and reduced back into lead ingots, whereafter it is refined and redistributed back to the Pb-acid battery manufacturers. When the crushed PP is separated from the other components of the lead-acid battery, the chips are extensively washed in order to eliminate any traces of lead-containing particles and acid which might have collected on its surface. The washed chips are then fed into an extruder where they are melted at approximately 245°C . The molten polymer is then pushed through a die (190°C) after which it solidifies and the extruded plastic is then pelletized. The high melting tempera-

ture of the extruder allows for complete mixing of all chips that originate from a variety of battery case types and speed up the recycling process. The flow diagram in Fig. 1 summarizes the recycling process of the lead-acid batteries.

Previous studies have shown that the reusability of the polymer is limited in terms of how often PP can be recycled [4]. It was shown that a simple lab technique such as a melt flow indexer (MFI) can be used to monitor the amount of recycled material present in a battery case if the MFI of the original virgin and recycled PP is known. The results were in agreement with other published studies in that the recycling of PP has a detrimental effect on the material's physical properties, such as impact and tensile strength, and also on its flow properties during injection molding [5–7]. A common practice in manufacturing is to blend recycled with virgin PP in order to maintain the integrity and physical properties of the final component. This reduces the detrimental effect of using recycled material and allows the use of relatively similar materials when sealing the cover to the battery case.

The waste recycling process is also regulated by the Environmental Protection Agency in terms of the volatile emissions generated during processing and the final disposal of the material, in particular VOCs and halogens [6]. If and when the spent recycled PP is considered as non-recyclable, it would either be disposed of as land-fill waste or incinerated. EU regulations have introduced the restrictions of hazardous substances directives (RoHS) and the waste electrical and electronic equipment directive (WEEE) that apply limitations of certain heavy metals present in plastic components and paints used by consumers. Guidelines are given for the recycling of the complete Pb-acid battery, but there are no clear directives for the requirements and environmental monitoring of various heavy metals found in the plastic components themselves that have become “non-recyclable”.

With the recent development of small-scale instrumentation, and the advancement of computer processing power, manufacturers of analytical equipment such as X-ray fluorescence (XRF) have developed portable small-scale instrumentation that allows for the analysis of samples in a quick and non-destructive manner. The instruments make use of small-scale X-ray tubes or radioactive isotopes to excite trace elements in a bulk matrix for their quantitative determination at concentrations levels as low as 10 ppm. The element is identified by its

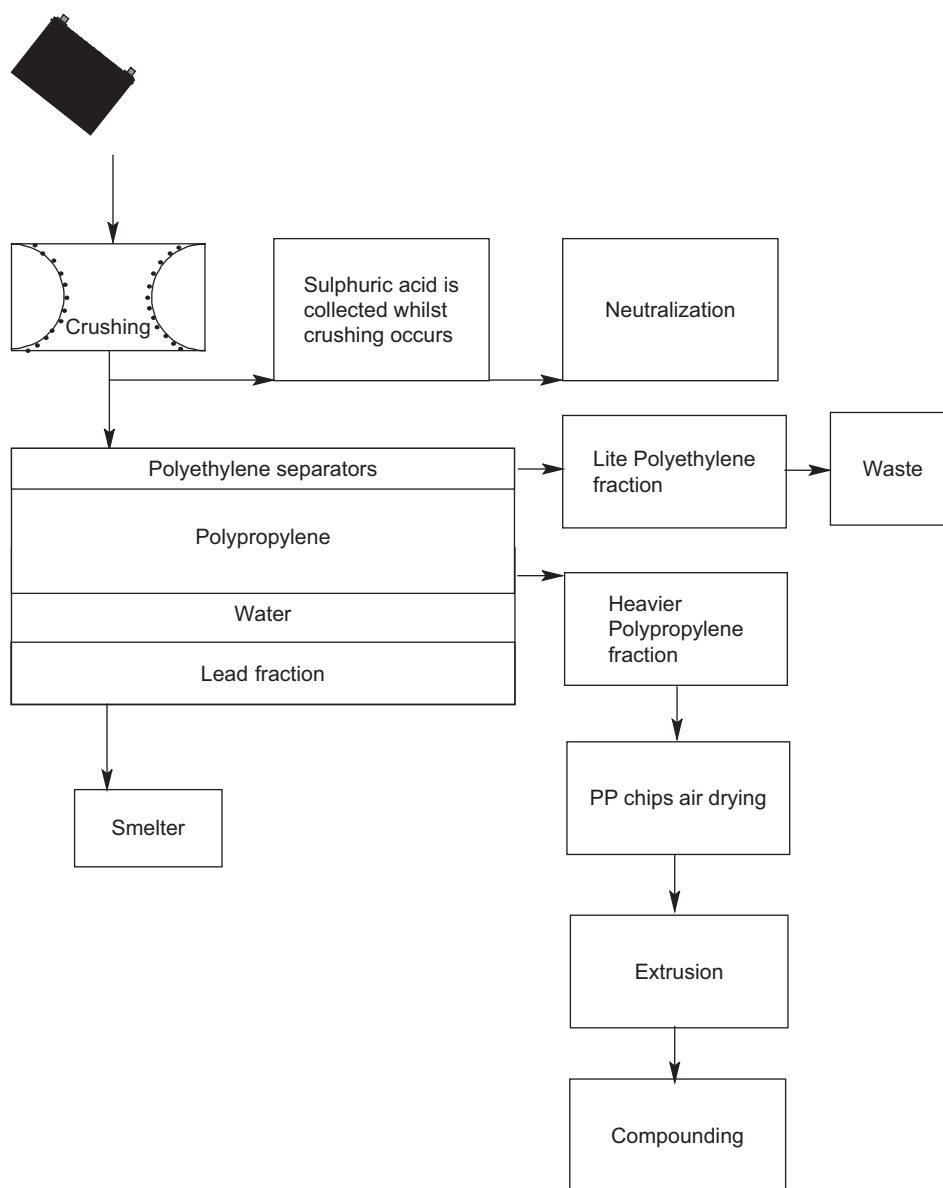


Fig. 1. A flow diagram illustrating the recycling process of the lead-acid battery.

characteristic X-ray emission wavelength (λ) or energy (E) and its quantification is done by measuring the intensity (I). Quantitative elemental analysis with XRF spectrometry is typically performed using empirical methods where calibration curves are obtained using standards that have similar properties to that of the unknown. The fundamental parameters (FP) approach is often preferred because it allows for the elemental analysis to be done without standards or calibration curves [8]. This enables the analyst to use the system immediately, without having to spend additional

time setting up individual calibration curves for the various elements and materials of interest.

XRF analysis of the battery case made with recycled PP showed that it contained significant amounts of Pb and other elements to merit an investigation into their effect on various properties of the plastic. The first part of the study aimed at accurately quantifying the elemental composition of the recycled PP and to establish a quick and easy non-destructive procedure to quantify future samples through the use of a portable XRF analyzer. The second part of the study investigated the

possible environmental effects that elements in particular Pb and Br contained in recycled PP would have during the injection molding process or the combustion or incineration of the plastic.

2. Experimental

2.1. Quantification of Pb and Ca detected by ICP and XRF in recycled PP

The quantification of Pb and Ca in recycled PP was done by comparing the results obtained by XRF analysis to a standard empirical technique of sample digestion and measuring the elemental concentration using ICP. Pre-weighed samples were ashed in a furnace at 500 °C for 4 h, after which the residue was digested with a mixture of nitric and hydrochloric acid. The samples were then filtered and diluted with deionized water. Standards of the elements analyzed (Pb and Ca) were prepared from 1000 ppm analytical grade stock solutions with the same acid concentration used for the preparation of the samples. Samples and standards were then analyzed on a Perkin-Elmer Sciex ELAN 6100 ICP-MS analyzer.

Standards for the XRF analysis were prepared by incorporating known amounts of Pb and Ca into wax that had similar matrix characteristics to that of PP. The method was described by Bichinho et al. for preparing molten wax standards with known amounts of a desired element obtained from a 1000 ppm stock standard solution [9]. However, when using the method for the preparation of wax standards with Pb and Ca, the sample preparation proved to be unsuccessful, in that a non-homogenous mixture of the elements in wax was obtained, with significant variations in the results between a top and bottom part of a wax pellet. As an alternative, the desired amounts of Pb or Ca in the form of PbSO_4 or CaCO_3 (that are commonly found in the recycled PP) were added to a pre-weighed granulated pure wax, after which the mixture was homogenized for 1 min in a liquid N_2 grinder resulting in a fine powder. The powder was pressed at about 400 kg/cm² into pellets at room temperature and their homogeneity was evaluated by taking at least two XRF scans for the respective elements on both sides of the pellets. A standard sample was accepted if the difference between the XRF readings between the two sides of the pressed pellet was less than 5%. At least five wax standards per element were prepared between

200 and 3000 ppm. The XRF analysis was done on an Innov-X XT-440L which was calibrated for a high sensitivity setting for trace elements found in the soil mode. Standard calibration curves for the Pb and Ca content in the wax were obtained and programmed into the analyzer software. Similar standards using the wax matrix were prepared for the elements of Ti and Br that are found in lower concentrations in the recycled PP.

The PP samples for the study were prepared from a mixture of recycled and virgin PP pellets that were sourced from two different recycling suppliers. Their sample preparation has been discussed previously [4]. The two types of material are described as a recycled PP with short-chained molecules with an initial MFI of 12.3 g/10 min and a recycled PP with medium-chained molecules with an initial MFI of 11.4 g/10 min. The virgin PP used was highly isotactic and had an initial MFI of 8.5 g/10 min. Samples were prepared by mixing ratios of 0%, 20%, 40%, 60%, 80% and 100% (by weight) of recycled and virgin material, respectively, using the two types of recycled PP. The comparative quantitative elemental analysis for Pb and Ca by ICP-MS and XRF were done on the samples by measuring the amount of Ca and Pb in the samples after completing the XRF instrumental calibration with the wax standard samples. The same samples were then prepared for ICP-MS analysis as described previously.

2.2. Volatility of Pb and Br during combustion of recycled PP

The investigation of the volatility of various elements found in the recycled PP during combustion or injection molding was done by placing a sample of recycled PP in a test tube that was connected to a trap that contained deionized water. The sample in the test tube was heated above 800 °C using a Bunsen burner and the resulting gases were allowed to bubble through the water. After complete combustion of the plastic sample, the aqueous solution was analyzed for Pb. An oily liquid that came from the burning process had formed on top of the water trap was also analyzed for its Pb content and characterized by FTIR on a Bruker Tensor 27. A qualitative analysis of the gases emitted during a typical injection molding process was done by heating a sample of recycled plastic to 230 °C for a few hours and allowing the gases that

are emitted to blow through a Pb-sensitive filter (Plumbtesmo[®]) and a solution of silver nitrate for the determination of Br. Hence, any gas vapors that contain Pb would give a color change on the filter paper, and any vapors that contain Br would precipitate as silver bromide, giving a qualitative indication of the elements present.

TGA analysis was done of a typical recycled PP pellet in order to quantify the amount of residue present. The analysis was done on a Mettler TGA SDTA51 and heating was done from room temperature to 800 °C at 10°/min under nitrogen and air, respectively. In order to identify the inorganic compounds present in the recycled PP, about 5 g of the material was ashed under nitrogen and air at 500 °C, respectively, and analyzed for their phase composition by X-ray diffraction on a Bruker D8 by scanning between 10° and 70° 2 θ at 0.02 steps at a scan rate of 2 s/step. The ashed sample in air was further heated to 800 °C and analyzed again by X-ray diffraction.

The particle sizes of inclusions in the recycled PP were studied by a Philips transmission electron microscope (TEM). Thin cross-sections of the material were viewed for any crystalline inclusions. Their elemental compositions were confirmed by EDS and their crystallinity confirmed by observing the electron diffraction pattern of the observed inclusions.

3. Results and discussion

3.1. Quantification of Pb and Ca detected by ICP and XRF in recycled PP

The initial semi-quantitative analysis for the type elements found in the recycled PP by XRF are shown in Table 1, together with the semi-quantitative XRF results of the ashed recycled PP at different temperatures which will be discussed later. Elements such as Cr, Ti, Br, Fe and Zn are used in coloring, stabilizers, flame retardants and fillers in the manufacturing of the battery cases and are noticeably of much lower concentration [10–13]. Elements such as Ca that are in higher concentrations come from the talc and CaCO₃ that are added as fillers and stabilizers to the plastics. Of significant interest was the high concentration of Pb found in the recycled PP. During the recycling process, where the crushed battery cases are washed, a significant amount of Pb in the form of PbO₂ and PbSO₄ remains on the surface of the plastic, becoming

Table 1

Summary of the semi-quantitative elements determined by XRF of a random batch of recycled PP and ashed samples

Element	Recycled PP before combustion (ppm)	After ashing, 500 °C (ppm)	After ashing, 800 °C (ppm)
Cr	100	890	2171
Fe	238	3288	8301
Zn	118	2113	12,288
Br	1188	3718	–
Pb	3247	44,911	> 10%
Ca	1727	66,646	> 10%
K	–	1812	7209
S	–	89,601	> 10%
Ti	725	21,136	48,266
Ba	140	867	2987
As ^a	400	–	–

^aAs is considered as an error due to overlapping of spectral peaks.

embedded into the polymer matrix during the high-temperature mixing stage.

The initial XRF analysis indicated that the recycled PP sample contained significant amounts of arsenic (400 ppm in italics in Table 1). However, no As was found after repeatable ICP analysis of the digested samples for the specific element. Upon closer inspection of the XRF spectra, it was noticed that the energy lines of Br and Pb interfered with the lines for As (Fig. 2). The energy K-lines for As (10.54 and 11.73 eV) overlapped with the L-line (10.55 eV) for Pb and the K-line (11.92 eV) for Br, respectively. This resulted in the instrument software interpreting the analysis results as if As were present in significant amounts. It is therefore important that careful inspection of the resulting spectra from simultaneous multi-elemental analysis by XRF is done for any possible overlapping and interferences of other elemental spectra lines.

The quantitative determination by ICP-MS was done for Pb and Ca on the two batches of recycled PP made with different concentrations of virgin PP. The results are shown in Figs. 3 and 4, with a good linear correlation between the amount of Pb and Ca found in the samples and the percentage of recycled PP.

The results also show that the concentrations of Pb and Ca vary between different batches and suppliers of recycled PP. The results for the Ca analysis showed that the graph did not go through the origin at 0% recycled PP. This could be due to a slight impurity and contamination of Ca from the

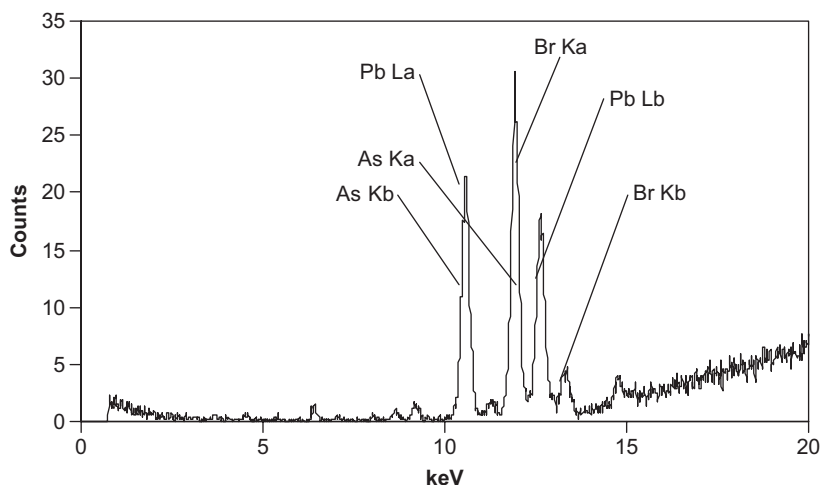


Fig. 2. XRF spectra of a typical recycled PP sample showing the spectra lines for Pb and Br overlapping with As.

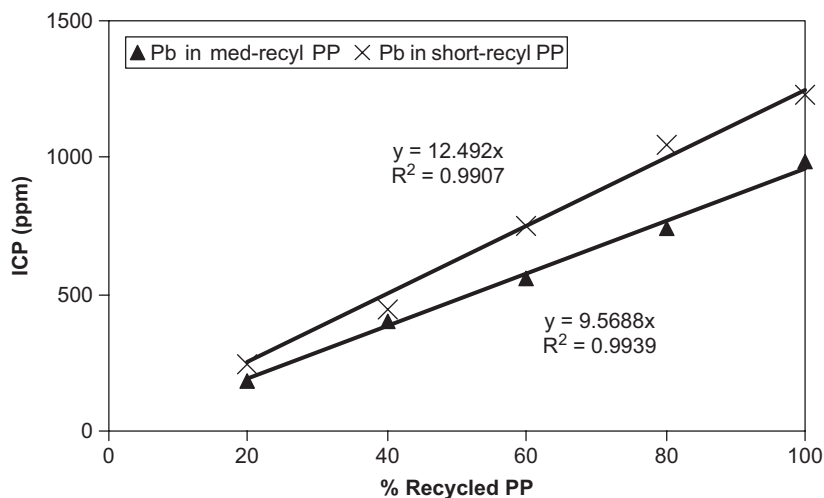


Fig. 3. Pb in recycled PP with medium- and short-chained recycled PP at various concentrations as determined by ICP.

distilled water and acid used during the sample preparation.

The calibration of the XRF instrument was done by preparing wax samples with known amounts of Pb in the form of PbSO_4 . The results show a good correlation of the values, and the slope of the graph obtained was programmed into the instrumental software before further analysis of the PP molded samples (Fig. 5). Similar standards were prepared for Ca using CaCO_3 . The slope of the graph was considerably different when compared to results obtained with the Pb samples (Fig. 6). Similar correlations were obtained for Ti and Br using the wax matrix as standards. The analysis of the four

elements in samples that were made with different amounts of recycled PP from two different batches are shown in Figs. 7 and 8, respectively. The results show that the concentrations of the four elements vary linearly with the amount of recycled PP used. Noticeably, the Br, Ca and Pb in the short-chained PP were higher than the corresponding samples made with the medium-chained recycled PP. The Ti contents in the two batches were relatively similar.

The comparison of the elemental analysis for Ca and Pb by XRF and ICP are shown in Figs. 9 and 10, respectively. The ICP analysis for Br and Ti were not considered since Br would become volatile during the ashing process of the plastic, and Ti

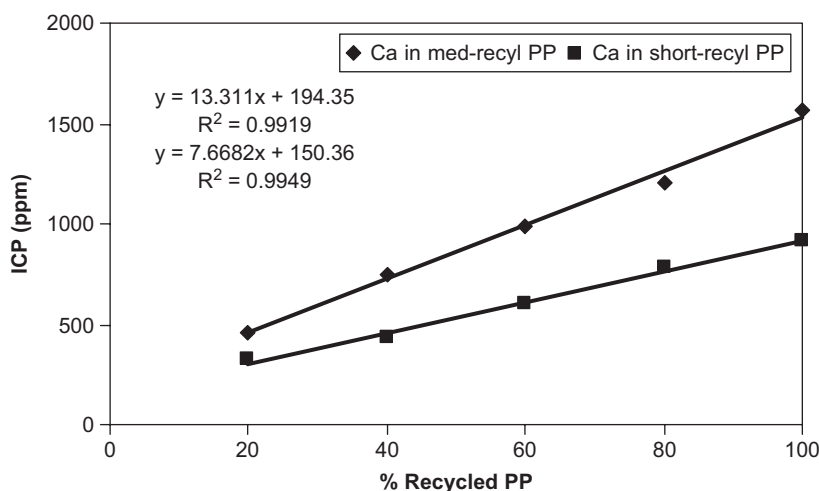


Fig. 4. Ca content in recycled PP with medium- and short-chained recycled PP at various concentrations as determined by ICP.

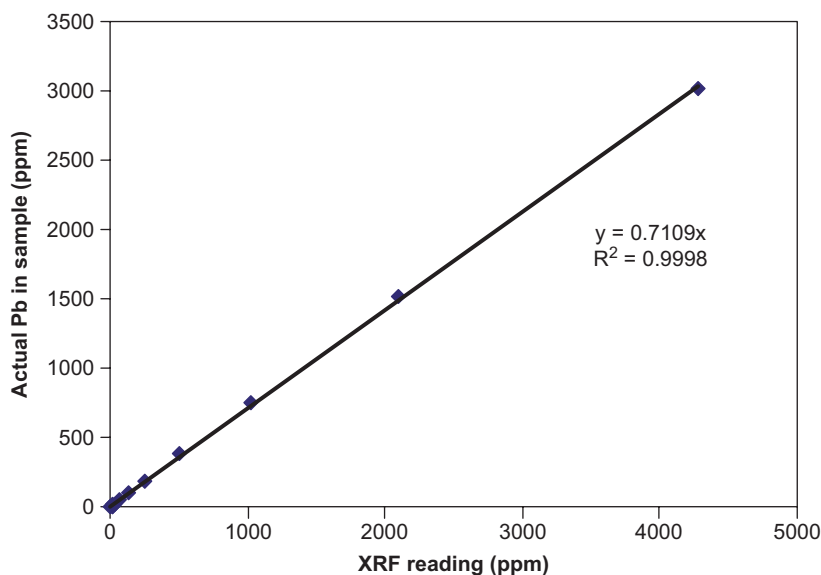


Fig. 5. The XRF correlation of standards prepared using wax with known amounts of Pb (in the form of PbSO_4).

would remain as TiO_2 and not dissolve easily in the acid solution used and, hence, be excluded during the filtering process.

The results showed a good correlation between the two different analytical techniques used for the two batches of recycled PP studied. The fact that the linear equations in Fig. 10 do not go through the origin can be attributed to the Ca contamination that occurred during sample preparation. However, the graphical slopes between the type or batch of recycled PP used and the ICP analysis were noticeably different. This disparity is amplified by considering the difference between the amounts of

Pb or Ca determined by XRF and that of ICP for each of the samples that have varying amounts of recycled PP (Figs. 11 and 12). Noticeably, the difference between the (XRF–ICP) values depends on the percentage of recycled PP and increases for both the short- and medium-chained recycled PP. The increase of (XRF–ICP) for Pb and Ca are comparatively higher for the samples containing the short-chained PP than the corresponding samples containing medium-chained PP.

The empirical method of elemental analysis by destructive ashing and digestion of a known amount of sample (plastic) and relating it to standards

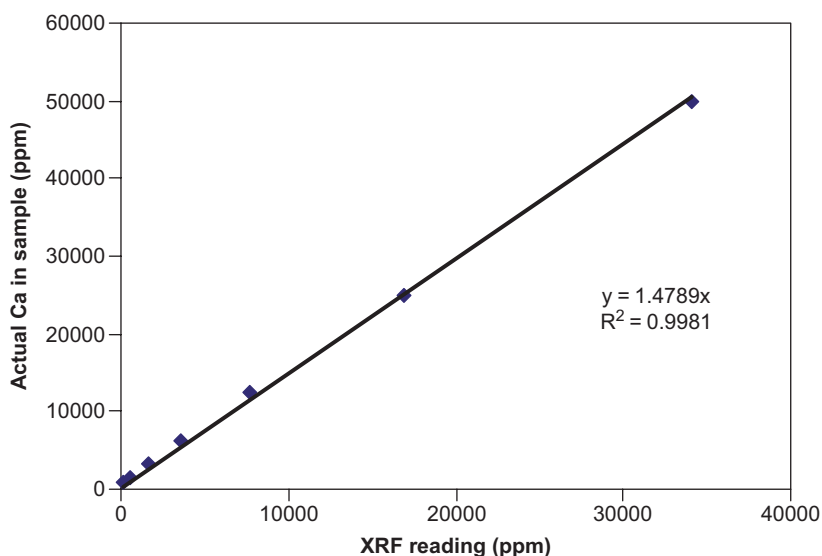


Fig. 6. The XRF correlation of standards prepared using wax with known amounts of Ca (in the form of CaCO_3).

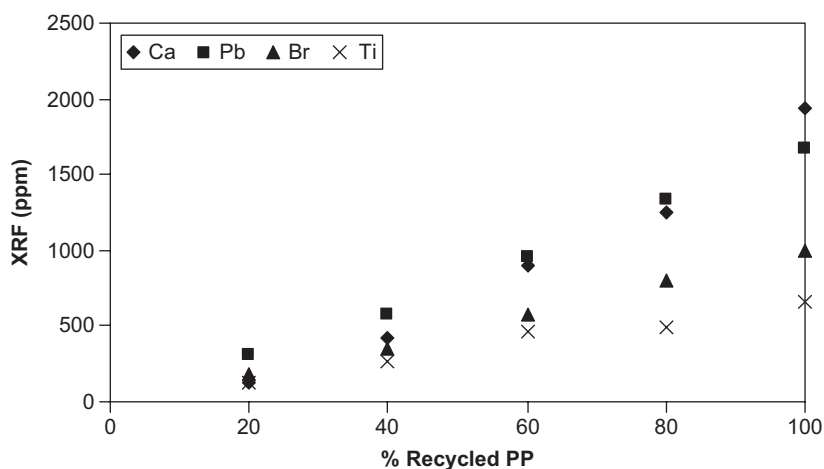


Fig. 7. Ca, Ti, Br and Pb found in short-chained recycled PP mixed with virgin PP as determined by XRF (ppm).

prepared of similar aqueous solutions is well known. The method completely destroys the organic matrix and considers all dissolved species of a particular element of interest. The influence of the variation of sample matrix between samples on the quantification results is considerably lessened. By comparison, the analysis of solid samples by XRF is quicker with less sample preparation time, covering a range of available elements of interest. However, the sample matrix composition is crucial and influences the accurate quantification of the elements of interest. If the matrices used are similar, wax or PP, and the elements of interest are of low enough concentration that they do not constitute

part of the main matrix, then relatively accurate quantification can be done by preparing suitable standards with a similar matrix. However, it is assumed that the types of recycled material received from various suppliers would be similar in terms of their main matrix composition (polypropylene). These results, however, showed that there is an influence on the XRF elemental determination by the batch type that would originate from different suppliers of the recycled PP. These differences could be in terms of the additives present such as organic stabilizers and flame-retardants of varying concentrations. Hence, the use of a wax matrix to obtain a good linear relationship between the XRF intensity

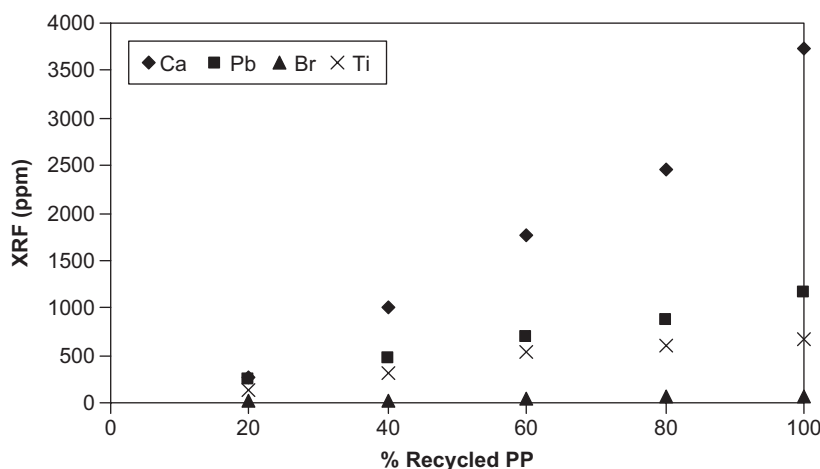


Fig. 8. Ca, Ti, Br and Pb found in medium-chained recycled PP mixed with virgin PP as determined by XRF (ppm).

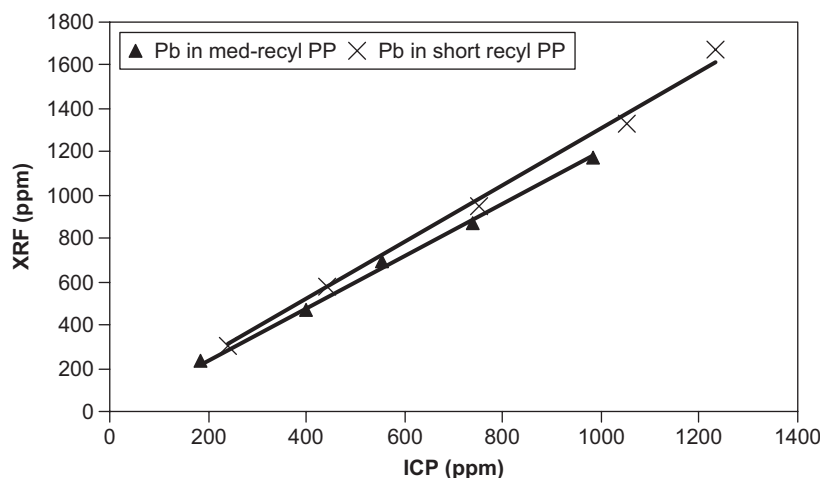


Fig. 9. The correlation between the amounts of Pb in the recycled PP as determined by XRF and ICP.

and the amount of a single element for the quantification of elements found in PP would not consider the matrix influence in its entirety. For example, the results showed that the amounts Br in the short-chained recycled PP that would originate from typical flame retardants was significantly higher in concentration, and its subsequent influence on the Pb or Ca content determination by XRF would be unknown. Hence, care should be taken in the interpretation of the quantitative multi-elemental composition of a recycled PP sample that contains various fillers and additives.

The amount of Pb (or other elements in significant amounts) in the recycled PP can be used as an indicator of the amount of recycled material used in a final molded sample that contained a

mixture of recycled and virgin PP. Even although the results showed that the accurate quantification of the elemental composition of the recycled PP by XRF is influenced by the other additives found in the particular batch, it should not influence the results, since it is a comparative study where the same batch of recycled PP is used for both the starting material and final molded product. The method can be used in combination with MFI as a procedure for determining the percentage of recycled PP in a battery case after injection molding [4].

As an example, both the MFI and the amount of Pb determined by XRF found in a certain batch of recycled PP and in the molded battery case made with the same batch is shown in Table 2. According

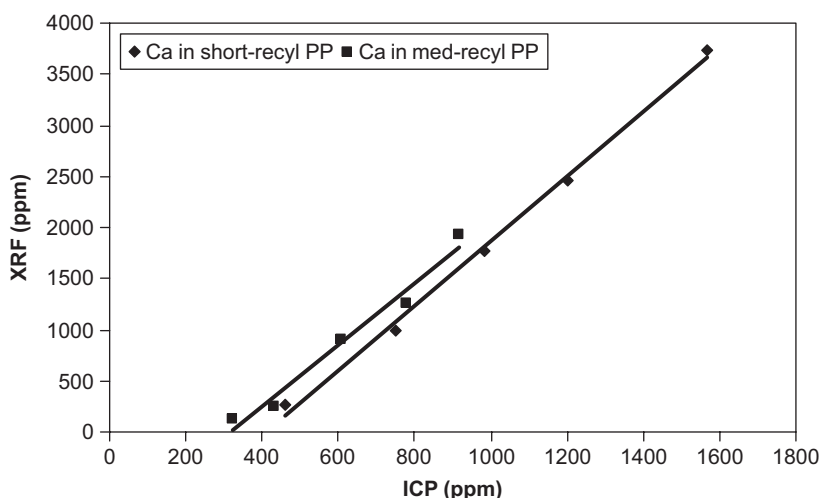


Fig. 10. The correlation between the amounts of Ca in the recycled PP as determined by XRF and ICP.

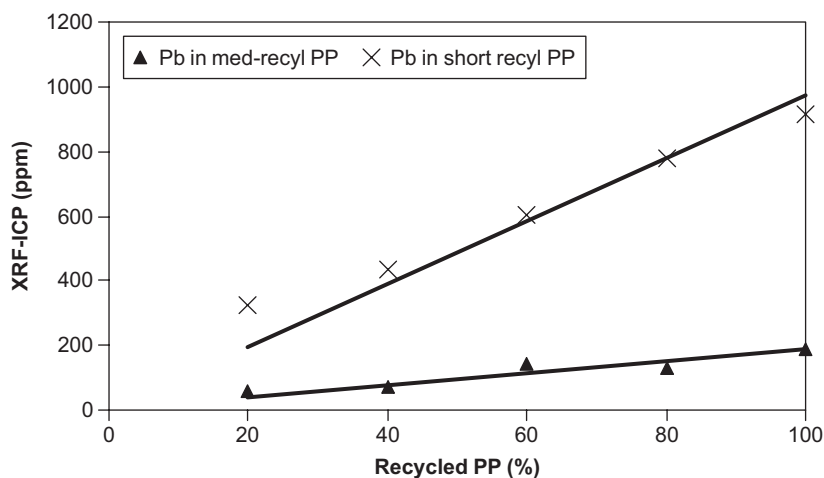


Fig. 11. Difference between the measured Pb by XRF and ICP versus the amount of recycled PP.

to the manufacturer, the battery case was made with 50% recycled PP. The results were in relatively good agreement with the manufacturer's specifications and that either MFI or XRF elemental analysis can be used as a method to determine the amount of recycled PP used in the manufacturing of battery cases. Hence, within a certain degree of accuracy, the verification of the amount of recycled PP used in molded samples can be determined. It is, however, important that the analysis of the raw starting material and the final molded product are done by the same calibrated instrument. The use of an XRF instrument is non-destructive and quicker in terms of analysis time when compared to the MFI technique, but considerably more expensive.

3.2. Volatility of Pb and Br during molding and combustion of recycled PP

The combustion of PP in air does result in the emission of VOCs that can prove to be hazardous to the environment [6]. In addition to the VOC products formed during burning, a number of hydrocarbon oils also become volatile during the high temperatures, and subsequently condense on cooling. This was observed by burning about 10 g of the recycled PP in a test tube and trapping the emitted gases in a water-trap test tube. FTIR analysis of the oily substance that collected on top of the water confirmed that it primarily contained long-chained hydrocarbons, some alkenes and

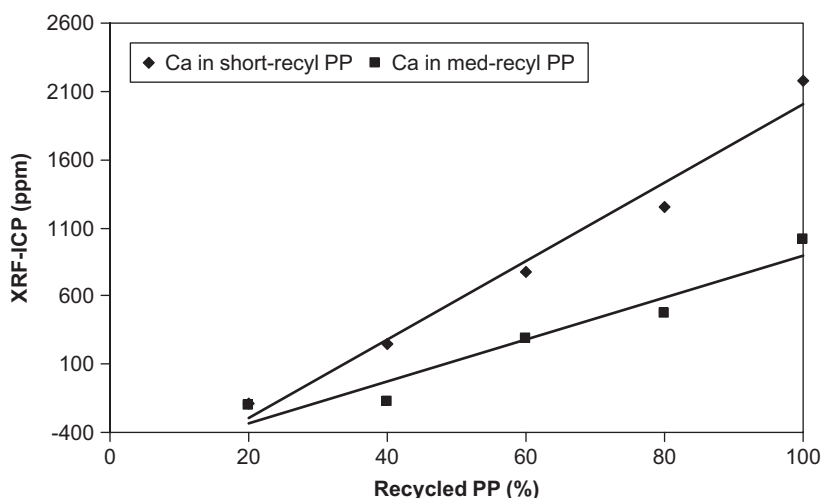


Fig. 12. Difference between the measured Ca by XRF and ICP versus the amount of recycled PP.

Table 2

The MFI and Pb (ppm) by XRF found in recycled PP and a battery case made with 50% recycled material from the same batch

Sample	MFI (g/10 min)	XRF Pb (ppm)
Recycled black PP pellets	12.19	1673
Virgin white PP pellets	7.08	0
Battery case	9.71	909
Predicted % recycled PP determined from MFI values	52	—
Predicted % recycled PP determined from XRF Pb values	—	54

carbonyl groups, which originated from the decomposition of the PP. The ICP analysis of the oily substance and water showed it to contain 0.52 and 0.14 ppm Pb, respectively. Hence, some Pb-containing particles are carried with the heated vapors during the combustion of the plastic. Small particles of below 1 μm can easily become “air-borne” with the slightest movement of air and also “stick” to small droplets of the larger organic volatile compounds and soot that is formed during the burning process.

The TGA analysis of the particular recycled PP showed that it contained about 3.5% residue. The decomposition of the material under N_2 gas and in air behaved similarly (Fig. 13). Noticeably, the decomposition (mass loss) under air would start at a lower temperature (216 °C), whereas under N_2 , it would start at about 290 °C. The decomposition of the recycled PP in air also showed a slight shoulder at about 333 °C, which could be due to partial oxidation of the material, that would then at higher temperatures decompose completely.

The semi-quantitative XRF analysis of the ashed sample obtained after burning the recycled PP at 500 and 800 °C showed it to contain a range of elements that are summarized in Table 1. The semi-quantitative XRF results were not adjusted according to its matrix composition, but can be considered as an indication of the change in elemental composition of the ashed sample after burning at different temperatures. The X-ray diffraction patterns of the ashed samples are shown in Fig. 14.

The results show that the sample heated at 500 °C in air and nitrogen contained talc (magnesium silicate), anglesite (PbSO_4), β - PbO_2 , rutile (TiO_2), Fe_2O_3 , CaCO_3 and possibly MgBr_2 . However, the sample when heated to 800 °C, contained significantly more CaSO_4 . It also contained TiO_2 , PbO_2 and lanarkite ($\text{Pb}_2(\text{SO}_4)\text{O}$) with the absence of any talc and MgBr_2 . The materials most probably became volatile or changed its phase composition at the higher temperatures, where the Mg could have originated from the original additives found in the recycled PP. Mg hydroxides are used in the

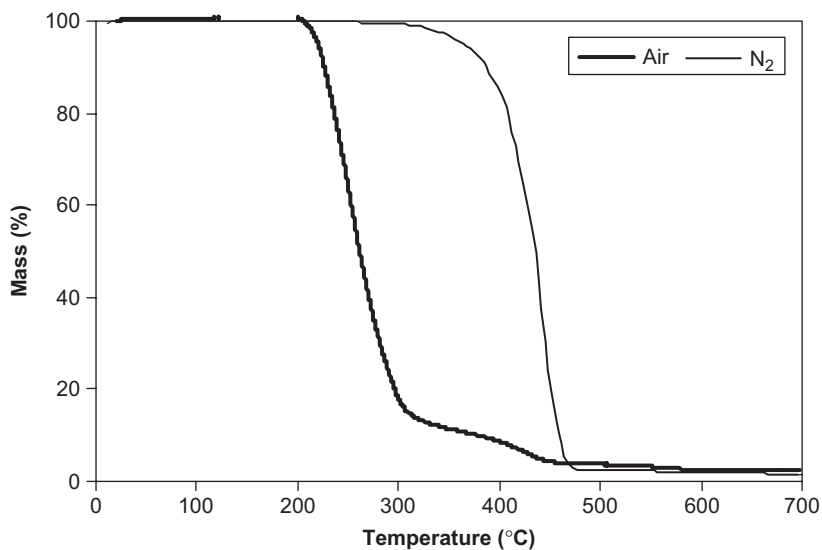


Fig. 13. The TGA analysis of recycled PP in N_2 and air, respectively.

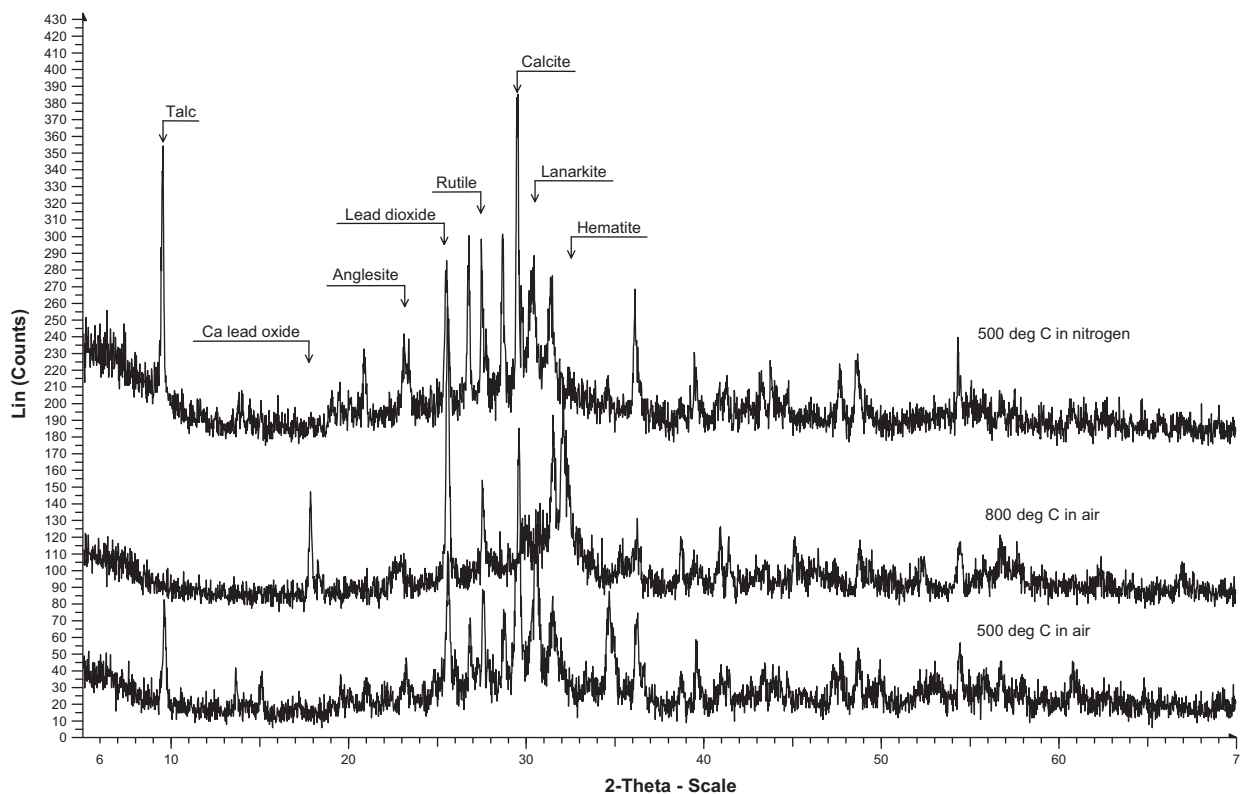


Fig. 14. X-ray diffractogram of the ashed sample at two different temperatures.

manufacturing of PP [13]. The Fe_2O_3 could have originated as a contaminant from the manufacturing process, where iron crushers are used in breaking up the battery cases. The $CaSO_4$ and Ca_2PbO_4

most probably formed from the reaction of the compounds present such as $CaCO_3$ and lead sulfate. $CaCO_3$ and talc are common fillers used in the manufacturing of PP [11,12].

The presence of lead (Pb) and other elements found in the recycled PP arises from the recycling process, where traces of Pb in the forms of PbO_2 and PbSO_4 originate from the battery content. It is highly unlikely that the elemental Pb found on the negative electrode would remain as pure Pb, since the metal oxidizes very easily when exposed to air. Tiny particles of the oxide and sulfate remain stuck on the surface of the crushed plastic during the washing process, after which it is incorporated and evenly distributed into the recycled PP pellet.

Transmission electron microscope analysis of a cross-section of the recycled PP is shown in Figs. 15a and b where small crystalline particles can be seen that are approximately 0.2–0.6 μm in

size. In one example, the EDS confirmed the presence of Ca, and the respective crystalline electron diffraction patterns of the inclusions are shown in the figures. The particles are most probably CaCO_3 , which was shown to be in relative large amounts from the X-ray diffraction study of the ashed samples.

The simulated qualitative analysis of the gases emitted during a typical injection molding process of PP at 230 °C for a few minutes showed that no Pb was present. The vapors were allowed to pass through a Pb-sensitive filter paper known as Plumbtesmo[®]. Any gas vapors that would contain Pb would give a color change on the filter paper, giving a qualitative indication that Pb does become air-borne during the molding process. No color change was observed implying that the heat generated during the melting process of the recycled PP is not sufficient to make the Pb-containing particles become “air-borne”. Only when combustion of the plastic takes place, there is enough air turbulence formed that allows the particles then to be carried with the movement of the volatile oil and soot generated by the burning process. The vapors that are formed from heating the recycled PP at 230 °C for a few minutes were allowed to bubble through a solution of silver nitrate. This resulted in a cloudy solution and the precipitation of AgBr. This is an indication that the Br found in recycled PP, which is typical of flame-retardants, does become volatile at injection molding or MFI testing temperatures. Care should therefore be taken to ensure that sufficient ventilation occurs near such equipment.

4. Conclusions

The study showed that significant levels of Pb and other elements are found in recycled PP. The Pb is in the form of PbO_2 and PbSO_4 and is incorporated as tiny particles (<1 μm) that come from the recycling process itself. The static attraction of the small particles on the plastic could prevent them from being effectively removed during the washing process. Other elements such as Ca, Ti, Br, Fe, Cr and Zn found in recycled PP, originate from a variety of fillers, additives, stabilizers, impurities and flame-retardants that are used in the battery case manufacturing.

The significantly high concentrations of Pb (or Ca) present in the plastic can be used as a type of “tracer” to determine the amount of recycled PP

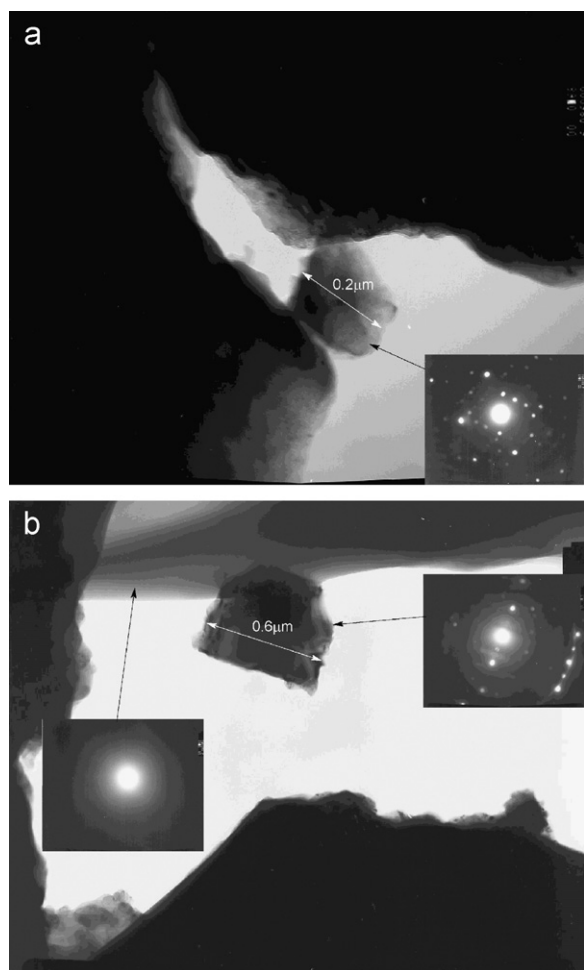


Fig. 15. TEM micrographs of small crystalline inclusions found in the polymer matrix. The inclusions' respective crystalline electron diffraction patterns are shown and are possibly identified as CaCO_3 . The electron diffraction pattern of the amorphous polymer region is also shown in part (b).

used in the manufacturing of a particular battery case. This is done by knowing the amount of Pb in the original recycled PP batch samples used in the molding of the battery cases. The amount of Pb in the recycled PP and battery case can be quickly measured with a non-destructive technique such as a portable XRF analyzer. Accurate quantification of the Pb (and other elements) by XRF is possible by preparing a range of suitable standards using wax as a matrix. The direct correlation of the elements to another technique such as ICP is influenced by the batch sample, which could have comparatively different additive concentrations. Care needs to be taken to ensure that the standard sample is completely homogenous with the added elements and all possible interferences are considered.

The Pb-containing particles are small enough to become air-borne during the burning of the plastic. Significant concentrations of Pb were found in the oily condensation products of the burned plastic and soot residue. The study also showed that Br becomes volatile at typical injection molding temperatures and is completely removed from the ashed samples at temperatures above 800 °C. Excessive exposure to halogenated compounds in the workplace is regarded as a health risk, and care should be taken to ensure sufficient ventilation near injection molding equipment.

The recycled PP used in the manufacturing of battery cases will eventually become “non-recyclable” and correct procedures for the disposal of heavy metal waste must be considered when battery cases that contain Pb are disposed of by land-fill waste or incineration. The burning process could cause significant amounts of very small Pb-containing particles to become air-borne, thereby becoming an environmental contaminant and health risk.

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References

- [1] H. Bode, *Lead Acid Batteries*, Wiley, New York, NY, 1977.
- [2] B. Bied-Charreton, Closed loop recycling of lead/acid batteries, *J. Power Sources* 42 (1) (1993) 331–334.
- [3] H. de Feraudy, Recycling the plastic components in today's lead/acid battery, *J. Power Sources* 42 (1) (1993) 315–318.
- [4] N. Rust, E.E. Ferg, I. Masalova, A degradation study of isotactic virgin and recycled polypropylene used in lead acid battery casings, *Polym. Test.* 25 (1) (2006) 130–139.
- [5] A. Valenza, F.P. La Mantia, Recycling of polymer waste: Part II—Stress degraded polypropylene, *Polym. Degrad. Stab.* 20 (1988) 63–73.
- [6] Q. Xiang, M. Xanthos, S. Mitra, S.H. Patel, J. Guo, Effects of melt reprocessing on volatile emissions and structural/rheological changes of unstabilized polypropylene, *Polym. Degrad. Stab.* 77 (2002) 93–102.
- [7] V.A. Gonzalez-Gonzalez, G. Neira-Velazquez, J.L. Angula-Sanchez, Polypropylene chain scissions and molecular weight changes in multiple extrusions, *Polym. Degrad. Stab.* 60 (1998) 33–42.
- [8] V.E. Buhrke, R. Jenkins, D.K. Smith, *A Practical Guide for the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis*, Wiley, New York, 1998.
- [9] K.M. Bichinho, G.P. Pires, F.C. Stedile, J.H.Z. dos Santos, C.R. Wolf, Determination of catalyst metal residues in polymers by X-ray fluorescence, *Spectrochim. Acta, Part B* 60 (2005) 599–604.
- [10] J. Kaspersmaa, C. Doumena, S. Munrob, A. Prinsa, Fire retardant mechanism of aliphatic bromine compounds in polystyrene and polypropylene, *Polym. Degrad. Stab.* 77 (2002) 325–331.
- [11] Y. Li, Q.F. Fang, Z.G. Yi, K. Zheng, A study of internal friction in polypropylene (PP) filled with nanometer-scale CaCO₃ particles, *Mater. Sci. Eng., A* 370 (2004) 268–272.
- [12] C.F. Cullis, M.M. Hirschler, T.R. Thevaranjan, Combinations of titanium(IV) oxide, iron(III) oxide and molybdenum(VI) oxide as flame retardants and smoke suppressants for thermoplastic polymers, *Eur. Polym. J.* 20 (9) (1984) 841–847.
- [13] G.I. Titelman, Y. Gonen, Y. Keidar, S. Bron, Discolouration of polypropylene-based compounds containing magnesium hydroxide, *Polym. Degrad. Stab.* 77 (2002) 345–352.